

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-110414

(43)Date of publication of application : 20.04.2001

(51)Int.Cl.

H01M 4/58
H01M 10/40

(21)Application number : 11-282445

(71)Applicant : NIPPON TELEGR & TELEPH CORP
<NTT>

(22)Date of filing : 04.10.1999

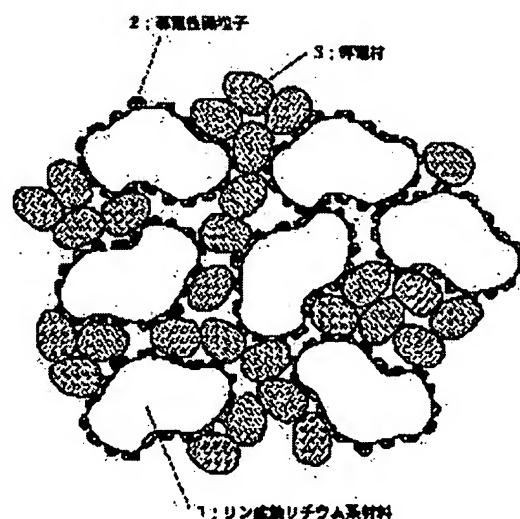
(72)Inventor : TAKAHASHI MASAYA
TOBISHIMA SHINICHI
TAKEI KOJI
SAKURAI YOJI

(54) MATERIAL FOR ACTIVATING POSITIVE ELECTRODE OF LITHIUM SECONDARY BATTERY AND THE LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance charging and discharging capacity of a lithium secondary battery during a large-current charging and discharging, where the lithium secondary battery uses a low-price material of iron phosphate lithium as a positive electrode.

SOLUTION: A powder 2 is carried on powder 1, where a powder 1 is formed of iron phosphate lithium series material having an olivine structure, which is indicated by the general expression $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, X is at least one selected from among magnesium, cobalt, nickel and zinc), while a powder 2 is formed of a material such that it has conductivity and whose oxidation-reduction potential is higher than that of a material for activating a positive electrode of a lithium secondary battery made of iron phosphate lithium series material. Therefore, a battery can be obtained which has larger charging and discharging capacity compared with others using an iron phosphate lithium series material that does not carry powders thereon, where charging and discharging capacity of the battery in relation to the invention is little decreased, even if charging and discharging current increases.



DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About lithium secondary battery positive active material and a lithium secondary battery, especially this invention is concerned with the conductive improvement in positive active material, and aims at an improvement of the discharge property in the high current of a cell, or a charge property.

[0002]

[Description of the Prior Art] The lithium secondary battery which uses as a negative-electrode active material a lithium metal, a lithium alloy, or the matter that emits [occlusion and] a lithium ion is characterized by the high electrical potential difference and the outstanding reversibility.

[0003] Using the multiple oxide of a lithium and transition metals especially as positive active material, since it is lightweight compared with the conventional lead rechargeable battery, a nickel-cadmium rechargeable battery, etc. and discharge capacity is also large, the rechargeable lithium-ion battery using the carbon system ingredient as a negative-electrode active material is widely used for electronic equipment, such as a cellular phone and a note type personal computer.

[0004] As positive active material of the rechargeable lithium-ion battery used for a current general ones, there are few reserves, and in order to produce the cobalt which is the raw material of LiCoO_2 although LiCoO_2 is mainly used only in the area moreover restricted, it is not desirable from the field of the price to the adequate supply of a raw material as positive active material of the rechargeable lithium-ion battery with which future more much more increment in need is expected.

[0005] On the other hand, it is shown clearly by JP,9-134724,A, JP,9-134725,A, Japanese Patent Application No. No. 261394 [11 to], etc. that the ingredient which permuted some iron of LiFePO_4 to which quantity of output used many cheap iron for the raw material, or LiFePO_4 by other elements operates as positive active material of a lithium secondary battery.

[0006]

[Problem(s) to be Solved by the Invention] However, these phosphoric-acid iron lithium system ingredients have the late insertion elimination reaction of the lithium at the time of cell charge and discharge, and since resistance overvoltage and activation overvoltage increase and the electrical potential difference of a cell falls when charge and discharge are performed with a big current, since electric resistance is large compared with lithium metallic oxides, such as LiCoO_2 moreover used conventionally, they have the problem that sufficient charge-and-discharge capacity is not obtained.

[0007] As an approach of solving such a problem, the particle of a phosphoric-acid iron lithium system ingredient is made detailed, and while increasing the area in which a reaction advances, it is possible that a current shortens distance which flows the interior of a phosphoric-acid iron lithium system ingredient particle.

[0008] However, the detailed particle of a phosphoric-acid iron lithium system ingredient is a lifting and a cone about secondary condensation, in case it mixes with electric conduction material at the time of electrode production. Inside a condensation grain, since phosphoric-acid iron lithium system ingredient particles touch at the small point and electric resistance becomes very large, with the active material of a condensation grain center section, even if it performs the charge and discharge of a cell, a reaction will not occur, but charge-and-discharge capacity will fall.

[0009] Therefore, it is made in order that this invention may solve the conventional technical problem mentioned above, and the purpose is in raising the charge-and-discharge capacity at the time of high current charge and discharge of the lithium secondary battery which used the cheap phosphoric-acid iron lithium system ingredient for the positive electrode.

[0010]

[Means for Solving the Problem] In order to attain such a purpose, the lithium secondary battery positive active material by this invention general formula $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 \leq y \leq 0.3$, $0 < z \leq 1$, and X: magnesium --) On cobalt, nickel, and the phosphoric-acid iron lithium system ingredient powder of the olivine structure given by at least one kind of zinc conductivity -- in addition -- and an oxidation reduction potential is characterized by supporting the powder of the **** matter rather than the oxidation reduction potential as lithium secondary battery positive active material of a phosphoric-acid iron lithium system ingredient.

[0011] moreover, the lithium secondary battery positive active material by this invention -- the aforementioned conductivity -- in addition -- and the matter more **** than the oxidation reduction potential as lithium secondary battery positive active material of a phosphoric-acid iron lithium system ingredient in an oxidation reduction potential

is characterized by being at least one kind of silver, carbon, platinum, palladium, gold, iridium, aluminum, titanium, and a tantalum.

[0012] Furthermore, the lithium secondary battery by this invention is characterized by including as an electrolyte the matter which can perform migration for a lithium ion to carry out [and] said positive active material, said negative-electrode active material, and electrochemical reaction including the lithium secondary battery positive active material mentioned above by using as a negative-electrode active material further the matter that emits [occlusion and] a lithium metal, a lithium alloy, or a lithium ion.

[0013] Drawing 1 is the mimetic diagram of a cross section which expanded some positive electrodes which mixed and produced the positive active material used for the lithium secondary battery by this invention, and electric conduction material. Even if the part which phosphoric-acid iron lithium system ingredient powder contacts directly by supporting the conductive particle 2 on the front face of the phosphoric-acid iron lithium system ingredient powder 1 is almost lost and makes small particle size of the phosphoric-acid iron lithium system ingredient powder 1 so that more clearly than this drawing, the condensation at the time of mixing with the electric conduction material 3 at the time of electrode production stops being able to happen easily.

[0014] Since the path of the current by the conductive particle 2 is formed in the interior of a condensation grain also when the phosphoric-acid iron lithium system ingredient powder 1 furthermore condenses and the active material inside a condensation grain fully comes to be used also when the electric resistance inside a condensation grain is reduced sharply and carries out the charge and discharge of the cell by the high current, the fall of the charge-and-discharge capacity by condensation of the phosphoric-acid iron lithium system ingredient powder 1 is inhibited.

[0015] Moreover, although strong resistance had arisen in the part with a small touch area in the conventional lithium secondary battery positive electrode since the big active material particles or active material particle, and electric conduction material particle of electric resistance touched directly Since the electric conduction material 3 touches conductive particle 2 comrades or the conductive particle 2 in the positive active material of this invention, while the resistance in the contact surface of an active material and the electric conduction material 3 becomes small By expansion contraction of the active material at the time of repeating the charge and discharge of a cell, while the energy loss at the time of change of resistance when a touch area changes also becoming small, and performing charge and discharge by the high current becomes small, capacity degradation accompanying charge and discharge also decreases. When such effectiveness compounds, it is thought by using the positive active material of this invention that the charge-and-discharge capacity at the time of the charge and discharge in the high current of the lithium secondary battery which used the phosphoric-acid iron lithium system ingredient for positive active material increases.

[0016] The phosphoric-acid iron lithium system ingredient of the lithium secondary battery positive active material by this invention is the phosphoric-acid compound of the olivine structure given by general formula $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$, $0 < y \leq 0.3$), and Element X is the stable matter electrochemically in the potential field of 3V to 4V to the standard potential of a lithium metal in the condition of constituting this phosphoric-acid compound. That is, X is at least one kind of magnesium, cobalt, nickel, and zinc. The olivine structure of LiFePO_4 is shown in drawing 2. The black dot shows Lynn where the tetrahedron was surrounded with four oxygen in the iron with which octahedron was surrounded with six oxygen in the lithium atom, respectively.

[0017] The above matter currently generally called the phosphoric-acid iron lithium is expressed with LiFePO_4 ($z = 1$, $y = 0$), and it cannot insert a lithium any more, with structure maintained. When this phosphoric-acid iron lithium system ingredient is used as a positive electrode of a cell, if it charges, a lithium will escape from a positive electrode and it will go, and if a presentation discharges the cell which approached FePO_4 (z becomes small) and charged it, the lithium in the electrolytic solution is inserted into a positive electrode, and the presentation returns to LiFePO_4 ($z = 1$). Although considering the discharge capacity of a cell, and production the ingredient of $z = 1$ is the most desirable, since the value of z changes continuously to this appearance, it can create to it the cell which operates by the device in which the matter of presentations, such as $z = 0.9$ which is an un-stoichiometric presentation, is also equivalent to the phosphoric-acid iron lithium of $z = 1$ which is the presentation of general stoichiometric. For this reason, inside of the above-mentioned formula and z It is shown by $0 < z \leq 1$.

[0018] While a lithium is desorbed from LiFePO_4 in the case of the charge, iron ion changes from divalent to trivalent. As a result of the desorption of the lithium, the crystal structure (olivine structure) of the part will become unstable, the moving trucking of a lithium will be closed partially, and the lithium which is in the interior further stops being able to **** easily. If some iron is electrochemically replaced by elements, such as stable zinc, in the potential field of 3V to 4V to the standard potential of a lithium metal by the condition of constituting the phosphoric-acid compound, even if it charges, permuted elements, such as zinc, will not oxidize in the divalent state, but will remain in a crystal, without being desorbed also from the lithium contiguous to the permuted element. For this reason, even if it charges, it is

thought that the part which permuted raises cycle stability while capacity increases, since a crystal structure cannot change easily and the moving trucking of a lithium is secured. However, since the lithium from which it is not desorbed does not participate in charge and discharge, if not much many such permutations are performed, the capacity of a cell will decrease. for this reason, the amount of permutations of the iron element with which the effectiveness of the increment in capacity is seen when permuting an iron element -- below 30% ($0 \leq y \leq 0.3$) -- desirable -- 10% - 30% ($0.1 \leq y \leq 0.3$) -- further -- desirable -- 10 - 20% ($0.1 \leq y \leq 0.2$) it is -- a thing is good.

[0019] this invention -- setting -- the conductivity of the above [front face / of a phosphoric-acid iron lithium system ingredient] -- in addition -- and an oxidation reduction potential makes a **** (high) conductive particle adhere rather than the oxidation reduction potential as lithium secondary battery positive active material of a phosphoric-acid iron lithium system ingredient This is because said conductive particle will produce electrochemical reaction previously, the dissolution by oxidation or a conductive fall will take place and the effectiveness of conductive particle support will be lost, if the potential from which the electrochemical reaction of a conductive particle occurs into lithium secondary electron is lower than the oxidation reduction potential (about 3.4 V) of a phosphoric-acid iron lithium system ingredient.

[0020] As such a conductive particle, it is desirable that it is at least one kind of silver, carbon, platinum, palladium, gold, iridium, aluminum, titanium, and a tantalum, for example. Although silver, palladium, and platinum were used as a metallic material and acetylene black was used as a carbon material as said conductive particle in the below-mentioned example, as a metallic material, gold, iridium, aluminum, titanium, a tantalum, etc. are sufficient. Moreover, as a carbon material, graphite and KETCHIEN black are sufficient.

[0021] As an addition of a conductive particle, in order that the unit weight as the whole positive active material or the discharge capacity per unit volume which combined the conductive particle with the phosphoric-acid iron lithium system ingredient may decrease if an addition is increased too much since this matter itself does not participate in a charge-and-discharge reaction, good ** RE **, especially 2% - 6% have 10 still more desirable% or less.

[0022] Moreover, as a particle size of a conductive particle, 1/10 or less [of the particle size of phosphoric-acid iron lithium system ingredient powder] is desirable, and 1/10 or less [1/100 or more] is especially desirable. As for a conductive particle, it is desirable that you are as small weight as possible and make it adhere to a phosphoric-acid iron lithium system ingredient powder front face uniformly in order not to participate in a cell reaction. For this reason, it is because there is a possibility of the amount of a conductive particle increasing too much and causing the fall of energy density when it is made to adhere to said phosphoric-acid iron lithium system ingredient powder front face uniformly when the particle size of a conductive particle becomes large.

[0023] In the further below-mentioned example, although what was cast to the pellet type as a positive electrode was used, a configuration like the spreading electrode which added positive active material and a binder like polyvinylidene fluoride to a solvent like N-methyl-2 1 pyrrolidone, produced the slurry, and carried out spreading desiccation of it thinly on the metallic foil is sufficient.

[0024] Moreover, although the lithium metal was used as a negative-electrode ingredient, otherwise, metal cull scorch nights, such as lithium transition-metals compound nitrides, such as metallic oxides, such as carbon system ingredients, such as a lithium alloy, a graphite, and corks, a tungstic-acid ghost, a niobic acid ghost, a banazin san ghost, and a stannic-acid ghost, a lithium manganese nitride, and a lithium cobalt nitride, a lithium iron nitride, an iron sulfide, and a molybdenum sulfide, etc. are sufficient.

[0025] Although the electrolytic solution which furthermore dissolved LiPF₆ in the equivalence mixed solvent of ethylene carbonate and dimethyl carbonate as the electrolytic solution at 1 mol/dm³ concentration was used, the same thing as the conventional nonaqueous lithium secondary battery is also usable.

[0026] For example, as a solvent, it is independent about dimethoxyethane, 2-methyl tetrahydrofuran, ethylene carbonate, methyl formate, dimethyl sulfoxide, propylene carbonate, an acetonitrile, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, etc., or it is possible to mix and use two or more kinds.

[0027] Moreover, LiClO₄, LiBP₄, LiAsF₆, and LiCF₃SO₃ grade are sufficient besides LiPF₆ used in the example as a solute. Furthermore, a polymer electrolyte, a solid electrolyte, ordinary temperature fused salt, etc. are usable.

[0028] Moreover, various well-known ingredients are conventionally usable about other elements, such as structural materials, such as a separator and a cell case. Although furthermore considered as the coin mold in the example also about the cell configuration, it may not be restricted especially and configurations, such as cylindrical and a square shape, are sufficient.

[0029]

[Example] Below, with reference to a drawing, the example of this invention is explained more at a detail. In addition, this invention is not limited only to the following examples.

[0030]

[Example 1] Drawing 3 is the cell sectional view having shown the configuration by 1 of the lithium secondary battery by this invention example. For a metal lithium negative electrode and 6, as for a positive-electrode case and 8, in drawing 3, a separator and 7 are [4 / a positive-electrode pellet and 5 / an obturation plate and 9] gaskets. The positive active material contained in the positive-electrode pellet 4 was produced by the following approach.

[0031] Diammonium hydrogenphosphate (NH_4) (2HPO_4) was mixed with the lithium carbonate (Li_2CO_3) which is a raw material about LiFePO_4 first, and ferrous oxalate 2 hydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) so that it might be set to 0.5:1:1 by the mole ratio, and it put into crucible, and compounded by calcinating at 800 degrees C under argon atmosphere for 24 hours.

[0032] Subsequently, LiFePO_4 powder compounded in the solution which mixed ethanol with water to 1:1 by the volume ratio was put in, and it fully stirred, and continuing stirring, weighing capacity was carried out and the silver nitrate (AgNO_3) was added so that the weight of the complex ion contained might turn into 5% of the weight of LiFePO_4 .

[0033] Furthermore, it is an acetaldehyde, continuing stirring AgNO_3 In addition, 20ml per g of silver was deposited on LiFePO_4 powder. Positive active material was produced by filtering this and drying.

[0034] The X diffraction chart of the obtained positive active material is shown in drawing 4. In addition to the peak of LiFePO_4 , the peak of the silver of the metal condition shown by * in drawing 4 was observed. Moreover, by electron microscope observation and EPMA measurement, the thing of the particle size of LiFePO_4 powder which about 1/ of particles of the silver of the particle size of 20 is doing for distributed support was checked on LiFePO_4 powder.

[0035] 5 % of the weight of polytetrafluoroethylenes which are 25 % of the weight of acetylene black and the binder which are 70 % of the weight of this positive active material and electric conduction material was kneaded, after rolling out with the biaxial roller what was used as the clay-like lump in thickness of about 0.6mm, it pierced to disc-like [with a diameter of 15mm] to punch, and the positive-electrode pellet 4 was produced.

[0036] Next, what carried out pressurization arrangement of the metal lithium negative electrode 5 on the obturation plate 8 made from stainless steel is inserted in the crevice of the gasket 9 made from polypropylene. Separator drawing 6 of the product made from polypropylene and microporosity and the positive-electrode pellet 4 are arranged in this sequence on a negative electrode. As the electrolytic solution the positive-electrode case 7 of the product made from stainless steel after carrying out optimum dose impregnation and infiltrating the electrolytic solution which dissolved LiPF_6 in the equivalence mixed solvent of ethylene carbonate and dimethyl carbonate at the concentration of 1 mol/dm³ -- covering -- by closing The coin mold lithium secondary battery with 2mm [in thickness] and a diameter of 23mm was produced.

[0037] It evaluated by performing charge and discharge on the conditions of constant current (charge termination electrical-potential-difference 4.0V, discharge-final-voltage 3.0V, 1mA, and 5mA with a big current) for the charge-and-discharge property of the produced cell.

[0038] The electrical-potential-difference curve at the time of discharging with a 5mA current is shown in drawing 5. The electrical-potential-difference curve is almost the same as that of the electrical potential difference at the time of carrying out the charge and discharge of the cell which used the phosphoric-acid iron lithium which is not supporting the conductive particle already known for the positive electrode, and used the lithium metal for the negative electrode with a small current, charge and discharge were performed by the oxidation reduction of iron ion, and it was checked that the oxidation reduction of the supported conductive ingredient has not happened.

[0039] The cases of discharge capacity where the cases of 1mA of currents were 5.6mAh(s) and 5mA of currents were 4.3mAh(s). The discharge capacity at the time of performing a charge and discharge test with each current value is shown in Table 1.

[0040]

[Table 1]

実施例及び比較例に示した電池の放電電圧と放電容量

実施例及び比較例	1 mA放電時の放電容量 (mA h)	5 mA放電時の放電容量 (mA h)
実施例 1	5. 6	4. 3
比較例 1	5. 2	3. 6
実施例 2	5. 7	4. 4
実施例 3	5. 4	4. 0
実施例 4	5. 5	4. 1

[0041]

[The example 1 of a comparison] LiFePO_4 which is the positive active material which does not perform support processing of the conductive matter was produced by the following approach.

[0042] Diammonium hydrogenphosphate (NH_4) (2HPO_4) was mixed with the lithium carbonate (Li_2CO_3) which is a raw material first, and ferrous oxalate 2 hydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) so that it might be set to 0.5:1:1 by the mole ratio, and it put into crucible, and produced by calcinating at 800 degrees C under argon atmosphere for 24 hours.

[0043] The positive-electrode pellet and the coin mold cell were produced by the same approach as an example 1 using the obtained positive active material.

[0044] When the same conditions as an example 1 estimated the charge-and-discharge property, the cases where the cases of 1mA of currents were 5.2mAh(s) and 5mA of currents were 3.6mAh(s), and discharge capacity had the large fall of the capacity at the time of only a discharge capacity smaller than an example 1 being obtained also when it is any, but examining especially by 5mA constant current.

[0045] The electrical-potential-difference curve at the time of discharging with a 5mA current is combined with the curve of an example 1, and it is shown in drawing 4 . Moreover, the discharge capacity at the time of performing a charge and discharge test with each current value is combined with the value of an example 1, and is shown in Table 1.

[0046]

[Example 2] The positive active material contained in a positive-electrode pellet was produced by the following approach.

[0047] Diammonium hydrogenphosphate (NH_4) (2HPO_4) was mixed with the lithium carbonate (Li_2CO_3) which is a raw material first, and ferrous oxalate 2 hydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) so that it might be set to 0.5:1:1 by the mole ratio, and it put into crucible, and calcinated at 350 degrees C under argon atmosphere for 5 hours.

[0048] Subsequently, after adding 10g per 1kg of raw materials of acetylene black (DENKI KAGAKU KOGYO make) and fully mixing, it produced by calcinating at 800 degrees C under argon atmosphere for 24 hours.

[0049] The positive-electrode pellet and the coin mold cell were produced by the same approach as an example 1 using the obtained positive active material.

[0050] When the same conditions as an example 1 estimated the charge-and-discharge property, discharge capacity with a discharge capacity bigger also when the cases where the cases of 1mA of currents are 5.7mAh(s) and 5mA of currents are 4.4mAh(s) and it is any than the example 1 of a comparison was obtained.

[0051] The discharge capacity at the time of performing a charge and discharge test with each current value is combined with the value of an example 1 and the example 1 of a comparison, and is shown in Table 1.

[0052]

[Example 3] The positive active material contained in a positive-electrode pellet was produced by the following approach.

[0053] Ferrous oxalate 2 hydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and diammonium hydrogenphosphate (NH_4) (2HPO_4) were mixed with the lithium carbonate (Li_2CO_3) which is a raw material about LiFePO_4 first so that it might be set to 0.5:1:1 by the mole ratio, and it put into crucible, and compounded by calcinating at 800 degrees C under argon atmosphere for 24 hours.

[0054] Subsequently, after fully stirring [after grinding LiFePO_4 compounded in the acetonitrile solution of acetic-acid palladium ($\text{Pd}_2(\text{OCOCH}_3)$)], it filtered and dried and $\text{Pd}(\text{OCOCH}_3)_2$ was made to adhere on LiFePO_4 powder.

[0055] This was calcinated at 250 degrees C under argon atmosphere for 5 hours, and positive active material was produced by supporting palladium with pyrolyzing $\text{Pd}(\text{OCOCH}_3)_2$ on LiFePO_4 powder.

[0056] The coin mold cell was produced by the same approach as an example 1 using the obtained positive active material.

[0057] When the same conditions as an example 1 estimated the charge-and-discharge property, discharge capacity with a discharge capacity bigger also when the cases where the cases of 1mA of currents are 5.4mAh(s) and 5mA of currents are 4.0mAh(s) and it is any than the example 1 of a comparison was obtained.

[0058] The discharge capacity at the time of performing a charge and discharge test with each current value is combined with the value of examples 1 and 2 and the example 1 of a comparison, and is shown in Table 1.

[0059]

[Example 4] The positive active material contained in a positive-electrode pellet was produced by the following approach.

[0060] Diammonium hydrogenphosphate (NH_4) (2HPO_4) was mixed with lithium-hydroxide 1 hydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) which is a raw material first, and ferrous oxalate 2 hydrate ($\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$) so that it might be set to 1:1:1 by the mole ratio, and it put into crucible, and calcinated at 800 degrees C under argon atmosphere for 24 hours, and LiFePO_4 was compounded.

[0061] Subsequently, it is LiFePO_4 to LiFePO_4 obtained powder. 6g [per 100g] platinum powder (300 meshes) was added, after mixing with a mortar, it put into the planet ball mill made from a pebble, and grinding mixing was carried out for 20 minutes, and distributed support of the particle of platinum was carried out on LiFePO_4 powder.

[0062] The coin mold cell was produced by the same approach as an example 1 using the obtained positive active material.

[0063] When the same conditions as an example 1 estimated the charge-and-discharge property, the cases of discharge capacity where the cases of 1mA of currents were 5.5mAh(s) and 5mA of currents were 4.1mAh(s). The discharge capacity at the time of performing a charge and discharge test with each current value is combined with the value of examples 1-3 and the example 1 of a comparison, and is shown in Table 1.

[0064]

[Effect of the Invention] the cell using the phosphoric-acid iron lithium system ingredient which does not support by using the matter which supported the particle which has conductivity on phosphoric-acid iron lithium system ingredient powder as positive active material according to the lithium secondary battery by this invention as explained above -- comparing -- charge-and-discharge capacity -- large -- in addition -- and even if it increased the charge and discharge current, it found out that a cell with little reduction of charge-and-discharge capacity was obtained.

[0065] therefore -- economical -- excelling -- in addition -- and it became realizable [a lithium secondary battery with a good cell property].

[Translation done.]